

AD-753 382

ELECTRONIC SPECTRA OF LARGE MOLECULES
AND CRYSTALS

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Prepared for:

Army Research Office (Durham)

1972

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Unclassified
Security Classification

AD-753 382

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of Pennsylvania		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP NA	
3. REPORT TITLE Electronic Spectra of Large Molecules and Crystals			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report: 1 July 1969 - 30 June 1972			
5. AUTHOR(S) (First name, middle initial, last name) Robin M. Hochstrasser			
6. REPORT DATE 1972		7a. TOTAL NO. OF PAGES 46	7b. NO. OF REFS
8a. CONTRACT OR GRANT NO. DA-ARO-D-31-124-G1115		8b. ORIGINATOR'S REPORT NUMBER(S) NA	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) 6455.7-C	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES None		12. SPONSORING MILITARY ACTIVITY U. S. Army Research Office-Durham Box CM, Duke Station Durham, North Carolina 27706	
13. ABSTRACT A main object of this work was to probe electronic properties of large molecules using low temperature spectroscopic methods and by studying the effects of external fields on high resolution spectra. The measurements of the Stark effect on the benzophenone crystal were completed. A Study of the singlet and triplet states of dichlorobenzophenone excitons in electric fields was completed. The dipole moment of the pyridine molecule in its lowest singlet ($n\pi^*$) state was determined. A Zeeman effect study of solid carbon disulphide was completed and showed the correctness of assignments based on applications of theory to gas phase spectra.			
14. KEY WORDS Low temperature spectroscopic methods Electronic spectra Large Molecules Crystals			

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U S Department of Commerce
Springfield VA 22151

AROD-6455.7-C

FINAL REPORT

1. ARO-D proposal number: DA-AROD - 31-124-G1115
2. Period covered by report: 7/1/69 - 6/30/72
3. Title of proposal: ELECTRONIC SPECTRA OF LARGE MOLECULES AND CRYSTALS
4. Grant number: 6455-C
5. Name of Institution: UNIVERSITY OF PENNSYLVANIA
6. Author of report: ROBIN M. HOCHSTRASSER
7. List of manuscripts published under AROD sponsorship
- a. "Excited State Dipole Moments of Benzophenone in Singlet and Triplet $n \pi^*$ States", R. M. Hochstrasser and L. J. Noe, Journal of Molecular Spectroscopy, Vol. 38, 1, pp. 175-180, 1971.
 - b. "Zeeman Effect in the Electronic Spectrum of Solid CS_2 ", Robin M. Hochstrasser and Douwe A. Wiersma, The Journal of Chemical Physics, Vol. 54, 10, pp. 4165-4169, 15 May 1971.
 - c. "Structural Sensitive Aspects of the Electronic Spectrum", Robin M. Hochstrasser, Probes of Structure and Function of Macromolecules and Membranes, Vol. 1, Probes and Membrane Function, pp. 57-64, 1971.
 - d. "Excited State Dipole Moment of Pyridine", Robin M. Hochstrasser and J. W. Michaluk, The Journal of Chemical Physics, Vol. 55, 9, pp. 4668-4669, 1 November 1971.
 - e. "Structure and Dipole Moment of the First Electronically Excited State of Pyridine N-Oxide", Robin M. Hochstrasser and Douwe A. Wiersma, The Journal of Chemical Physics, Vol. 55, 11, pp. 5339-5343, 1 December 1971.
 - f. "Reassignment of the $n \rightarrow \pi^*$ Transitions of Phthalazine", Robin M. Hochstrasser and Douwe A. Wiersma, The Journal of Chemical Physics, Vol. 56, 1, pp. 528-530, 1 January 1972.

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AD 753382

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The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

- g. "Optical and Electric Field Effects in the Singlet and Triplet States of the Dichlorobenzophenone Crystal", Robin M. Hochstrasser and J. W. Michaluk, Journal of Molecular Spectroscopy, Vol. 42, 1, pp. 197-202, April 1972.

8. Scientific personnel supported by this project and degrees awarded:

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J. W. Michaluk, Ph.D. 1972
J. D. Whiteman, Post-Doctoral
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9. Outline of Research Findings:

A main object of this work was to probe electronic properties of large molecules using low temperature spectroscopic methods and by studying the effects of external fields on high resolution spectra.

The measurements of the Stark effect on the benzophenone crystal were completed. The dipole moments of the lowest ³ nπ* and ¹ nπ* states were obtained, by means of our Stark effect method, and found to be $\mu(^1n\pi^*) = 1.46 \text{ D}$, $\mu(^3n\pi^*) = 1.79 \text{ D}$. These values assume a ground state moment of 2.98 D, but the experimental value of $\Delta\mu_T/\Delta\mu_S$ (relative value of singlet and triplet dipole moments) is 0.78, and this is not dependent on ground state data. We believe this ratio is less than unity because it should be less difficult to separate two electrons in orthogonal orbitals when their spins are antiparallel.

A study of the singlet and triplet states of dichlorobenzophenone excitons in electric fields was completed. We achieved the first second-order Stark effect experiments on molecular solids in the study of the triplet exciton of this crystal: What was a single transition at zero-field became two exciton lines in the presence of an electric field. Our results suggest that this technique may be useful in probing anisotropic features of energy transfer processes by simultaneously examining the trap emissions and the exciton absorptions for different field directions. We also found $\Delta u_S = 1.29 \pm 0.06$ D and $\Delta u_T = 0.68 \pm 0.05$ D, again showing that $\Delta u_S > \Delta u_T$ for an aromatic ketone.

We have determined the dipole moment of the pyridine molecule in its lowest singlet ($\pi\pi^*$) state. This was done by measuring the energy of interaction between the dipolar molecules, dispersed in a single crystal of benzene at 1.6° K, and an external electric field. The result, $\Delta\mu = -3.2 \pm 0.1$ D, is confirmatory of traditional qualitative notions regarding the effect of promoting a nonbonding electron into an antibonding π - orbital. On the contrary, for pyridine N-oxide we have shown that $\Delta\mu = +0.71 \pm 0.03$ D for the lowest state, thereby demonstrating that this state is benzene-like $\pi\pi^*$. In both these systems (pyridine in benzene and pyridine - N - oxide in dichlorobenzene) we have used Stark effects to determine the orientation of the impurity molecule in the host

lattice, and in both cases the guest and host molecules are not aligned in any simply predictable fashion. These results present a challenge to the theory of the intermolecular forces that determine the orientations.

In other work we have completed a Zeeman effect study of solid carbon disulphide that showed the correctness of assignments based on applications of theory to gas phase spectra.

These studies have contributed greatly to our understanding of electronic processes in large molecules in the condensed phase, and they are a necessary adjunct to more mechanistic studies concerned with electronic behavior and relaxation in molecular crystals.